International Journal of Engineering Research (ISSN : 2319-6890)
Volume No.2, Issue No. 7, pp : 462-466 01 Nov 2013

Control of Molecular Weight Distribution in Batch Emulsion Polymerization using PID Controller: Case Studies

Parul Arora, Alok Gupta
Chemical Engineering Department, Malaviya National Institute of Technology, Jaipur (Rajasthan), India
Email : parul.arora07@gmail.com

Abstract : ***Two Control strategies are developed to control the molecular weight in emulsion polymerization by manipulating flow-rates of water stream of jacket in first case study and the power of heater in another study. The control strategies were validated with experimental data of emulsion polymerization using Methyl methacrylate as monomer. PID controller is used to control the temperature of the reactor in both the case studies.***

Keywords- PID, Molecular weight, Heat load, manipulative variable.

Introduction

A batch polymerization is multivariate and non-stationary process, direct online control of polymer properties is not feasible. Few variables are available in batch process which can be measured directly for example temperature, pressure and flow rate of water stream of jacket.

We used temperature as a controlled variable in our study. Emulsion polymerization is an exothermic reaction, as the reaction proceeds temperature of the reaction mixture is also increases. Control of reaction temperature or temperature profile is crucial for the process safety and product specification for the reason that reaction temperature has an effect on final polymer properties. The reactor temperature is a balance between the heating time, the propagation rate constant, the initiator dissociation constant, and the heat removal capabilities of the reactor to control the temperature each and every one parameter should keep in mind. The class of instruments usually used for measurement are: Thermocouples, resistance thermometer and filled bulb thermometers.
On-line measurement of the MWD would be possible through the use of automated gel permeation chromatography (GPC), but although experimental setups capable of performing this task for solution polymerization have been reported (Ponnusvamy 1988),(Budde U. 1988) ,(Ellis 1988). The lack of hardware sensors might be overcome by software sensors, namely by estimating the MWD from the available on-line measurements of other variables. Although some success has been obtained in solution polymerization systems (Jo 1976),(Schuler 1986) ,(Ellis 1988) ,(Adebekun and Schork 1989), the compartmentalized nature of emulsion polymerization generally speaking makes the MWD non observable from usually available on-line measurements (monomers conversion and temperature). Nevertheless, under some circumstances of practical significance, the MWD of the emulsion polymer is not affected by the compartmentalization of the system.

Authors (Ibrahem S Altarawneh 2009) developed an online calorimetric method monitoring the evolution of conversion and molecular weight in complex polymerization reactors (Vicente, Leiza et al. 2003).
The calorimetric model was validated offline for batch and semi-batch emulsion polymerization of styrene with and without transfer agents. The conversion was validated using offline gravimeter. The molecular weights measured offline via size exclusion chromatography with multiple detectors compared well with those estimated online using the calorimetric method. They found that a semi-batch emulsion polymerization process can be controlled online to approach living polymerization involving transfer agents. Thus that model was suitable as a 'soft-sensor' for real-time control applications.
A batch polymerization process is multivariate and non-stationary, direct online control of polymer properties is not feasible, so we develop control strategies using matlab. Three moments for live and three for dead polymer chain were used in our kinetic model taken from literature. These moments explained the distribution of the molecular weight (Shahrokhi and Fanaei 2002; Smeets, Heuts et al. 2009; Storti, Polotti et al. 1992).

Design of controller

The polymerization kinetic model explained above was simulated in matlab. The PID controller was first used in 1939 and is the most widely used controller in the market till today. PID controller is a feedback controller as shown in figure 1 below, using a block diagram representation. As shown in the figure, the process is the objective to be controlled. The purpose of the control is to make the process variable y follow the set-point r. To achieve the purpose, the manipulative variable u is changed by the controller.

$$G_c = K_p\left(1 + \frac{1}{sT_i} + T_d s\right)$$
$$= K_p + \frac{K_i}{s} + K_d s$$

First controller strategy used is split range and second is heat load. Split range is a controller configuration where a single PID controller outputs to two control valve. In our case PID output signal controls the hot-water and cold water steam as per required. As shown in fig.2 below how the hot water and cold water streams changes with output signal. The range of signal is constrained between 0-1.Flow rates are used as manipulative variable and reactor temperature is used as control variable.

In second strategy heat load is used as manipulative variable, which may vary from 40-140 W in our case optimum value is 90W. Heat load value is highly correlated with flow rate

of stream. The generated results were first compared with experimental data and then further proceeds towards comparison of strategy.

Before implementing the controller tunning parameters should be optimised first to achieve the good performance of the controller. The parameters were optimized and used given in table no-3.

Result and Discussion

Particle size distribution of the emulsion polymer or product is convincingly influence polymer's rheological, chemical, physical, mechanical, film forming properties.

Batch reactor was used for production of PMMA.A measured amount of MMA, emulsifier and water was charged to the reactor. The reactor was bubbled with nitrogen gas to purge oxygen from the reactor. The reactor was brought to the initial temperature and then required amount of initiator was supplemented to the reactor. Comparison of experimental value of reactor temperature with simulation without controller and with controller was studied and the result found was shown below in fig 3. PID controller is successfully operated; performance of controller was studied with different parameters. After this we compared two methods which will be explained later.

In our study first strategy uses split range controller as explained above and second one uses heat load as a manipulative variable. In the split range controller, the reactor is initially heated with hot water until the reaction begins to generate heat. Then cold water is used. Figure 2 shows how the flow rates of cold and hot streams change with output signal of the controller.

Both two are capable to maintain the desire reactor temperature with load changes and suddenly set point changes. Performance index is calculated for the system, results are discussed in table no 4 and 5.The comparison of result of the controller, experimental result and without a controller is given in fig.3

The Green line is showing the heat load method and blue shows split range. As clearly shown in fig 4 split range controller requires minimum time to settle down at set-point i.e 343K and heat load takes ample of time (4000 sec) but there are small oscillations in split range controller. Split range controller uses both hot water stream and cold water stream as its manipulative variable (fig 5) and is not capable to maintain set-point better than heat load. The performance index for both the controller were studied and discussed in table 4.As the data of Performance index provide evidence that heat load perform better than the split range, fig 5 shows the flow rates of hot water and cold water stream in the split range controller. The hot stream temperature is 380 K and temperature of cold stream used is 294K.The maximum flow rates of the streams is 0.5 kg/s. The value of Absolute error for split range is 3.7613e+007 which is enormously higher than the heat load method having value 8.9167e+006..Both the controllers behave well at load change and set-point change in system. Performance index were compared in table 5.A contradictory results were found. Performance index shows heat load as manipulative variable is capable to handle set-point change better than split range, which means heat load as manipulative variable is much better strategy to be used since physically or practically there may be load at any time to the controller. A better controller is who handle the load change and set-point change efficiently along with set-point. Figure 6 and 7 shows set-point change in both the controllers. In split range after set point change there are some oscillations before settling down on change but in heat load set point change is very smooth.

In this study we calculate error with adjustable parameters then select the optimum value of parameter with minimum error. These set of parameters are tabulated in table no-6.

The tunning of the temperature controller is an important issue, Low controller gain leads to overshoot, Kc=1 leads to 8K overshoot and at Kc=3 leads to 3K overshoot as shown in fig.

Higher the value of TauI leads to oscillatory response of the controller as shown below in the figure. A comparison of molecular weight is given in figure which demonstrate that molecular weight of polymer is main tined at the value 12500 gm/mol with the help of controller rather than of without controller.

Table 1: Energy balance for split range controller.

Process energy equation	$\rho V C_P \frac{dT}{dt} = \Delta H R_P - h_i A_i \left(T - T_M \right)$
Energy equation for metal wall	$\rho_M C_{PM} V_M \frac{dT_M}{dt} = h_i A_i \left(T - T_M \right) - h_{os} A_o T_M - T_J$
Energy equation for hot water	$V_J \frac{dU_J \rho_J}{dt} = F_S \rho_S H_S - h_o A_o \left(T_J - T_M \right) - W_C h_C$
Energy equation for cold water	$C_J \rho_J V_J \frac{dT_J}{dt} = F_W C_J \rho_J \left(T_{J0} - T_J \right) - h_o A_o \left(T_M - T_J \right)$
Energy equation for jacket	$\frac{dT_J}{dt} = \frac{F_{hot} T_{hot} + F_{cold} T_{cold}}{V_J} - \frac{\left(F_{hot} + F_{cold} \right) T_J}{V_J} + \frac{U A_J (T_R - T_J)}{V_J \rho_J C_J}$

Table 2: Energy balance for controller having heat load as manipulative variable.

Equation for Reactor	$Q+(-\Delta H)R_m V-UA(T-T_J)/VC_p\rho-(T/VdV/dt)$
Jacket dynamics	$M_cC_{pc}(T_{ji}-T_{jo})+UA(T-T_j)/V_c\rho_cC_{pc}$

Table 3: Control parameters.

Parameter	Split range	Heat load
Kc	0.1	9
TauI	0.0009	0.01

Table 4: Performance at set-point (343 K) using two different control strategy

Performance Criteria	ITAE	IAE	ISE	ITSE
Split range controller	3.7613e+007	4.6035e+003	6.1616e+004	4.6702e+006
Controller using heat duty	8.9167e+006	1.2244e+004	1.5136e+005	3.5224e+007

Table 6: Performance of controller using heat duty as manipulative variable

Parameters	ITAE	IAE	ISE	ITSE
Kc-9	7.7540e+007	1.4355e+004	1.4409e+005	3.1997e+007
Kc-6	7.9275e+007	1.8180e+004	1.9122e+005	5.2
Kc-3	8.4318e+007	2.8848e+004	3.4146e+005	1.5
Kc-1	9.6242e+007	4.5368e+004	6.5680e+005	5.3
TauI-0.0001	1.6711e+008	1.1272e+004	1.4334e+005	2.2
TauI-0.001	7.7540e+007	1.4355e+004	1.4409e+005	3.1
TauI-0.01	8.9167e+006	1.2244e+004	1.5136e+005	3.5
TauI-0.1	1.3334e+007	1.9443e+004	3.0616e+005	1.2

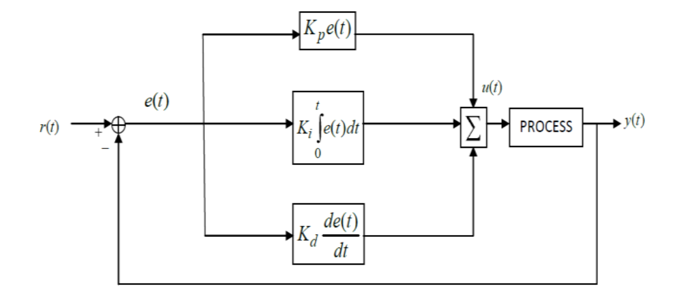


Fig 1: PID control Logic

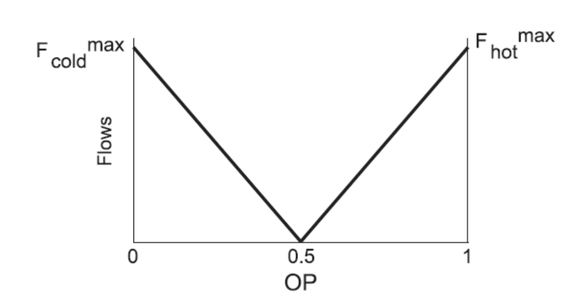


Fig 2: Slit range temperature control (manipulative variables Vs control signal).

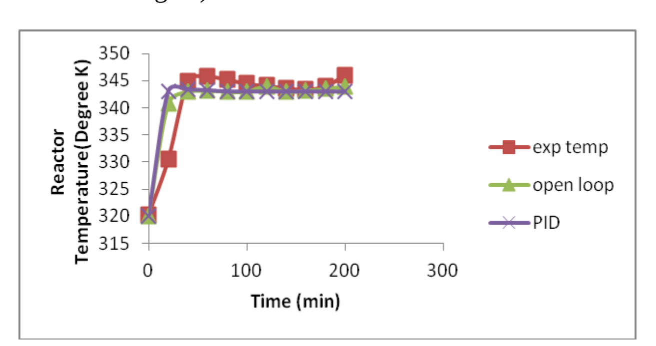


Fig 3: Comparison of Reactor Temperature.

Fig 4: Control Variable (split range- blue, Heat load- Green).

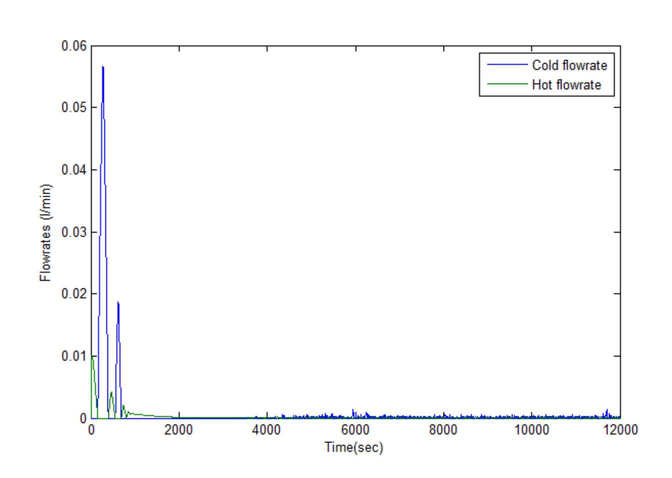


Fig 5: Hot and cold stream for split range controller.

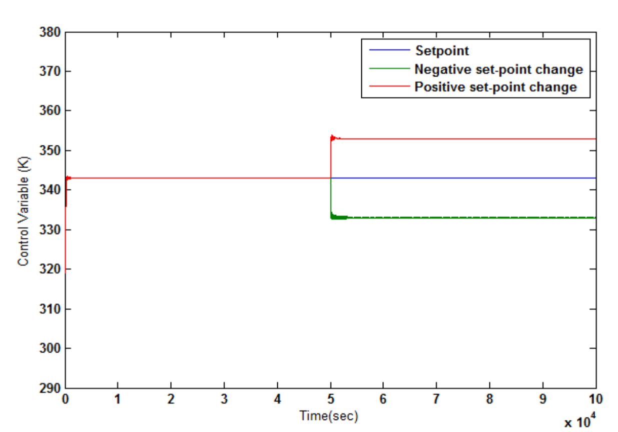


Fig 6: Set point change in split range controller.

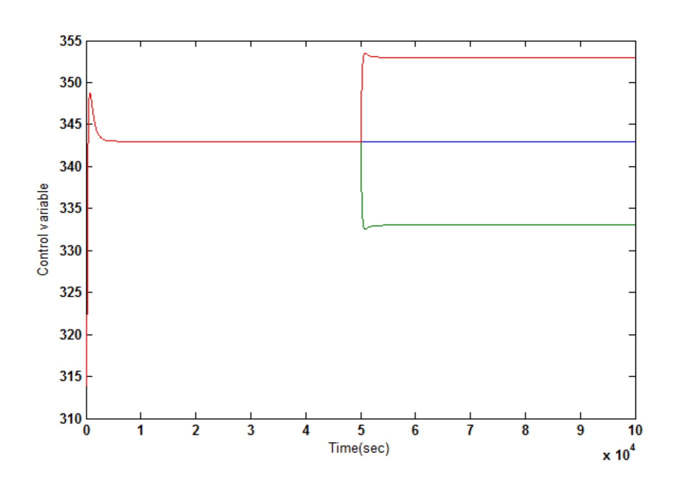


Fig 7: Set point change in second controller (heat duty as manipulative variable).

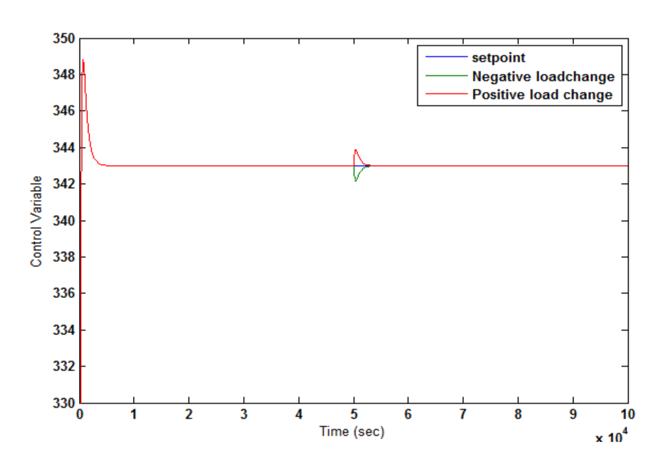


Fig 8: Load change in second controller (heat duty as manipulative variable).

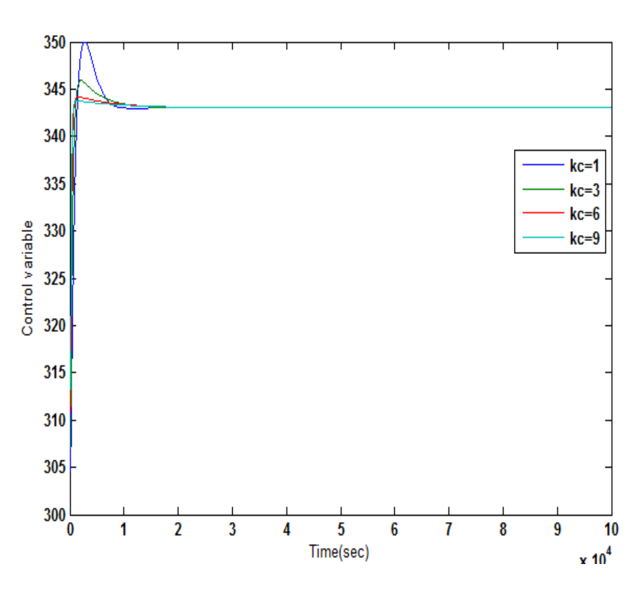


Fig 9: Analysis of controller gain in second controller.

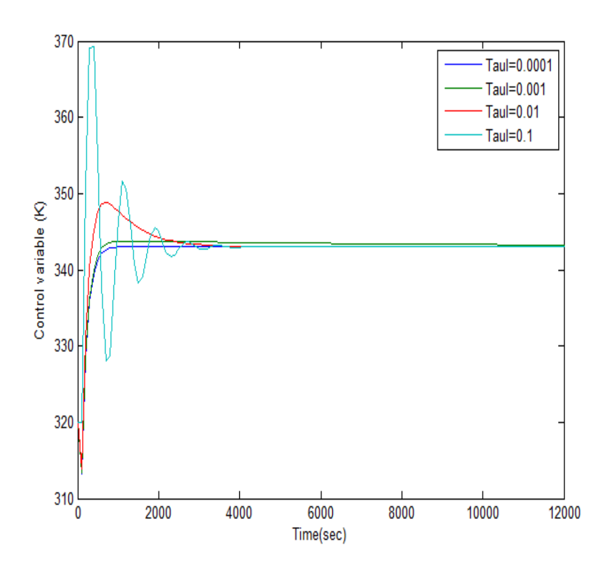


Fig 10: Analysis of TauI in second controller.

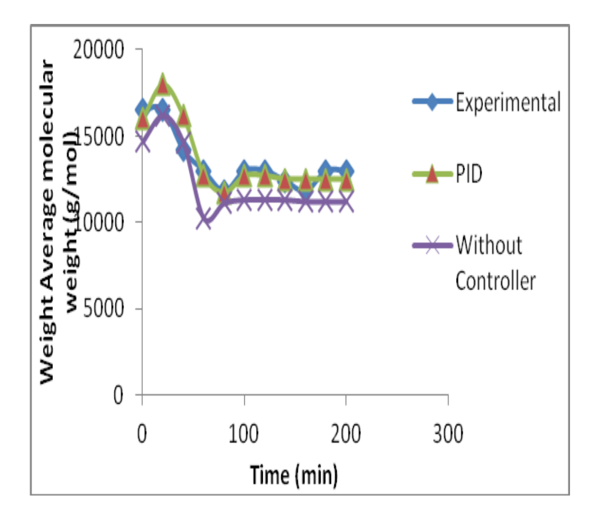


Fig11: Comparison of experimental data with controller.

References

i. Adebekun, D. K. and F. J. Schork (1989). "Continuous Solution Polymerization Reactor Control. 2. Estimation and Nonlinear Reference Control during Methyl methacrylate Polymerization." *Ind. Eng. Chem. Res.* **28**: 1846-1861.

ii. Budde U., a. K. M. R. (1988). "Automatic Polymerization Reactor with On-Line Data Measurement and Reactor Control." *Angew.Mukromol. Chem.* **161**.

iii. Ellis, M. F., T. W. Taylor, V. GonzBlez, and K. F. Jensen (1988). "Estimation of the Molecular Weight Distribution in Batch Polymerization." *AIChE J.* **34**: 1341

iv. Ibrahem S Altarawneh, V. G. G., Mourtada H Srour (2009). "Online polymer molecular weight and conversionmonitoring via calorimetric measurements in RAFT emulsion polymerization." *Polym Int in Wiley Interscience* **58**: 1427-1434.

v. Jo, J. M., S. 0. Bankoff, (1976). "Real Time Estimation of Polymerization Reactors." *AIChE J* **22**: 361.

vi. Ponnusvamy, S., L. L. Shah, C. khparissides, (1988). "On-Line Monitoring of Polymer Quality in a Batch Polymerization Reactor." *J. Appl.Poly. Sci* **32**: 3239.

vii. Schuler, H., S. Papadopoulou, (1986). "Real Time Estimation of the Chain Length Distribution in a Polymerization Reactor: 11. Comparison of Estimated and Measured Distribution Functions." *Chem.Eng. Sci*. **41**: 2681.

viii. Shahrokhi, M. and M. A. Fanaei (2002). "Molecular Weight Control of a Batch Suspension Polymerization Reactor." *Iranian Polymer Journal* **11**(6): 404-411.

ix. Smeets, N. M. B., J. P. A. Heuts, et al. (2009). "Mass Transport Limitations and Their Effect on the Control of the Molecular Weight Distribution in Catalytic Chain Transfer Mediated Emulsion Polymerization." *Macromolecules* **42**: 6422–6428.

x. Storti, G., G. Polotti, et al. (1992). "Molecular Weight Distribution in Emulsion Polymerization. ." *J. Polym. Sci., Part A: Polym. Chem.* **30**: 731-740.

xi. Vicente, M., J. R. Leiza, et al. (2003). "Maximizing production and polymer quality (MWD and composition) in emulsion polymerization reactors with limited capacity." *Chemical Engineering Science* **58**: 215-222.

Table 5: Performance of controllers for set point chan change and load change.

Controller	Split Range controller				Controller using Heat duty			
Parameter	ITAE	IAE	ISE	ITSE	ITAE	IAE	ISE	ITSE
Positive Load Change	2.2805 e+006	190.6 399	3.5205 e+003	4.2102 e+007	5.9895 e+007	1.3246 e+004	1.5194 e+005	6.4684 e+007
Negative Load change	2.7642 e+006	231.1 174	4.2346 e+003	5.0635 e+007	5.9942 e+007	1.3246 e+004	1.5191 e+005	6.2928 e+007
Positive set-point change	4.8527 e+010	364.3 028	5.0364 e+003	6.6920 e+011	3.7366 e+010	5.1037 e+005	5.1328 e+006	3.7362 e+011
Negative set-point change	1.5279 e+010	315.2 05	2.09 e+003	2.1469 e+011	3.7366 e+010	5.1037 e+005	5.1328 e+006	3.7362 e+011